# PATENT SPECIFICATION

RECEIVED CENTRAL FAX CENTER

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NO DRAWINGS

Inventors: JOSEPH PARK and MALCOLM GORDON STEWART

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### COMPLETE SPECIFICATION

## Improved Film-Forming Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to film-forming compositions modified by the inclusion of fluorinecontaining ester to enhance their stain resistance and oil, stease and water repellency

containing ester to enhance their stain resistance and oil, grease and water repellency.

Film-forming polymeric materials such as, for example, cellulose esters and others, polymethyl methacrylate, polyvinyl acetate or polyvinyl chloride are commonly used in lacquer compositions for surface coatings. We have now discovered that films having enhanced resistance to staining and improved oil and grease repellency may be obtained by mixing certain fluorme-containing esters with the film-forming polymeric material in the lacquer or film-forming composition.

Thus in accordance with the invention a film-forming composition comprises a film-forming polymeric material and a fluorine-containing ester containing a chain of at least three carbon atoms in which at least half of the carbon valencies other than carbon to carbon are satisfied by a fluorine atom, the quantity of ester being such that the fluorine content of the composition is in the range 0.1 to 30%, and preferably 1—2%, by weight of the total solids.

The fluorine-containing chain may be provided by either the acid or the alcohol from which the ester is derived or both portions may contain a fluorine-containing chain. A convenient ester, in which the fluorine containing chain is provided by the acid pornion of the ester, may be derived from a fluorine containing carboxylic acid of the formula RP—COOH wherein RP denotes a fluorinated alkyl group. Preferably the R' group is a straight or branched chain alkyl group of 4 to 18 carbon atoms in which at least half, and preferably all, of the hydrogen atoms are replaced by fluorine atoms. Convenient R' groups include perfluorobutyl and perfluoroheptyl and a bis-(2-permafluoroethyl)-2-trifluoromethyl ethyl group. The fluorine-containing esters may conveniently be estern of the acids RP-COOH with a mono- or polyhydric alcohol. Preferred alcohols include castor oil, ethylene glycol, polyethylene glycol, glycerol, tri-methylolpropane, trimethylolethane, mono-and dipentacrythritol, trimethylol amino methane and diethylene glycol monoether.

A convenient ester, in which the fluorine-containing chain is provided by the alcoholic portion of the ester, may be derived from a primary, secondary or terriary alcohol. Alcohols of the formula R<sup>2</sup>(CH<sub>2</sub>,0H, wherein R<sup>2</sup> denotes a fluorinsted alkyl group and n is an integer from 1 to 3, give especially useful compositions. Preferably the R<sup>2</sup> group in the above formula is a straight or branched chain alkyl group of 3 to 18 carbon atoms

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wherein at least half, and preferably substantially all, of the hydrogen atoms are replaced by fluorine atoms. Conveniently the R' group may be perfluoropropyl, perfluorobutyl, perfluorobutyl, perfluoroctyl or perfluorodecyl group. The fluorine-containing esters are conveniently esters of these alcohols with any of the aforementioned fluorine-containing carboxylic acids or with any other inoring carboxylic acids or with any other inoringanic or carboxylic acids (or the anhydrides or halides of such acid). Suitable acids include, for example, phosphoric, phthalic, adipic, sebacic, tartanic, citric, stearic and abietic acid and the adduct of abietic acid and maleic anhydride. The esters formed from polybasic acids may, if desired, be partial esters although completely esterified compounds are preferred.

The preferred film-forming polymeric materials include nitrocellulose, cellulose acetate, cellulose acetate butyrate, ethyl cellulose, polymethyl methacrylate, polyvinyl chloride and polyvinyl acetate, and copolymers there-

In addition to the polymeric film-forming material and the finorine-containing ester, the film-forming compositions may contain other modifying ingredients such as are commonly used in film-forming compositions. These include plasticisers, edip agents, and-sentling agents, pigments, resina and waves. The film-forming compositions may be prepared as lacquer solutions by dissolving in solvents, and applied to surfaces such as of wood, paper, 5 leather or metal, by brushing, spraying or other spreading means to give, on drying, a film having enhanced stain and soil resistance and oil, grease and water repellency.

The invention is further illustrated by the 40 following Examples in which all parts and percentages are by weight.

iges are of weight.

EXAMPLE 1

The nitrocellulose used in this Example had a nitrogen content 11.6 and 12.2% and was 'damped' with isopropanol in the ratio 70 parts nitrocellulose to 30 parts isopropanol. 40 g. of this nitrocellulose dried and dissoived in 100 cc. aqueous acetone, prepared by mixing 95 volumes acetone and 5 volumes water, bad a viscosity of 8 to 13 poises at 20°C.

Resin A was a non-drying coconut oil modified glyceral phthalate resin containing 31% fatty acid, 46% phthalic anhydride and having an acid value of 14.5 to 23.5 mg. KOH/

Resin B was a butylated urea/formaldehyde resin ("Beetle" (Registered Trade Mark) BE 640) used as a 60% solution in butanol.

Preparation of fluorine-containing ester
68 parts of pentacrythritol, 207 parts of
pentadecaffuorooctanoic acid and 20 parts of
xylene were mixed in a stirred reaction vessel
fitted with a Dean and Stark apparatus and

a gas inlet. Carbon dioxide gas was passed in at a rate of 10 cc. per minute and the temporature raised to reflux and maintained thereat for 1 hour.

The vessel contents were cooled to 100°C, 84 parts of acetic anhydride added, and a porous thimble containing anhydrous sodium sulphate placed in the reflux line. Hearing was resumed and reflux maintained for a further 5 hours.

Xylene and excess acetic anhydride were removed under vacuum to give 285 parts of pentacrythritol triacetate monopentaileca-fluorocctanoate (43%, fluorine) as a white waxy solid.

Lacquer preparation

The ester prepared above was incorporated into a lacquer having the following composition:—

	Parts	
Nitracellulose	24 (as dry)	
Resin A	36	85
Resin B	30	
Di-isooctyl phthalate	9	
Pentaerythritol triacctate		
mononermdecaffuorooctano	-	
ate (43% F) (as prepared	_	90
above)	1	
Dibutyl and monobutyl ac	ūď	
phosphates (Equimolar mix	; <del>-</del>	
ture)	3	95
Solvent	200	9.3

The solvent composition was: ---

	Parts	
Butyl acetate	30	
Ethyl acctate	18	
nabutanol	~- <b>12</b>	100
66 O.P. Industrial	l Methylated	
Spirits	4	
Xylene	15	
Tohiene	· 15	
Ethylene glycot mo	noethyl	105
ether	6	

The lacquer was sprayed on to a wood substrate to give a film. This film showed improved soil, water and grease resistance when compared with films made from the 110 same formulations omitting the fluorine-containing ester.

Example 2

Preparation of fluorine-containing ester
14.8 parts of phthalic anhydride, 117.0
parts of alcohol of formula H(CF<sub>2</sub>), CH<sub>2</sub>OH
and 40 parts xylene were mixed in a stirred
vessel fated with a reflux condenser and gas
inlet. Carbon dioxide was passed in at a rate
of 10 cc. per minute and the temperature
raised to reflux and maintained thereat for
12 hours

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5	The product was isolated by removing the xylene under vacuum to give 102 parts of fluoroalkyl phthalate as an off-white waxy solid containing 60% fluorine.  Lacquer preparation  The ester prepared above was incorporated into a lacquer having the following composition:	Parts Nitrucellulose (as used in Example 1) Resin A (as used in Example 1) Di-isooctyl phthalate Fluoroalkyl phthalate containing 46.6% F (as prepared above) Solvent  Parts  40 (as dry)  40 14 Fluoroalkyl phthalate containing 46.6% F (as prepared above) 6 Solvent 150	60
10	Parts	The solvent composition was:	
	Nitrocellulose (as used in Example 1) 24 Resin A (as used in Example 1) 36 Resin B (as used in Example 1) 36	Buryl acetate 9 Ethyl acetate 25 n-buranol 5 Toluene 50	70
15	ample 1) 30 Di-isooctyl phthalate 8 Fluoroalkyl phthalate com-	Isopropanol 11  The lacquer was sprayed on to a heavy	
20	taining 60%, F (as prepared above)  Dibutyl and monobutyl acid phosphate (Equimolar mixture)  Solvent  200	cardboard and showed superior soil, water and grease resistance when compared with a film made from the same formulation but omitting the fluorine-containing esters.	75
25	The solvent composition was:—	Preparation of fluorine-containing ester 13.45 parts of tricthylene glycol, 34.22 parts of perfluorocctanoyl chloride and 10.0	80
	Butyl acetate 30 Ethyl acetate 18 n-butanol 12 66 O.P. Industrial Methyl-	parts of pyridine were heated with 50 parts of toluene in a stirred reaction vessel fitted with a reflux condenser. The temperature was raised to reflux and maintained thereat for 10 hours. The contents of the vessel	85
30	ated Spirits 4 Xylene 15 Tolucne 15 Ethylene glycol monoethyl ether 6	were cooled and extracted with water until free from pyridine hydrochloride. Toluene was removed under vacuum to give 35.5 parus of triethylene glycol monopenradeca-fluorocctanoate as a pale yellow liquid of fluorine content 49.6%.	90
35	The lacquer was sprayed on to wood and gave a film of improved soil, water and greese resistance as compared with a film made from the same formulation but omitting the fluorine-containing ester.	Lacquer preparation The product prepared above was incorporated into a lacquer having the following composition:  Parts	95
40	EXAMPLE 3 Preparation of fluorine-containing enter 29.6 parts of phthalic anhydride, 146 parts of alcohol of formula H(CF <sub>2</sub> ) <sub>0</sub> CH <sub>2</sub> OH and	Nitrocellulose as used in Example I except that the viscosity of the solution of 40 g. (dry) in equeous acet-	100
45	0.1 g. of p-tolucae sulphonic acid were mixed	one was between 30 and 50 poises at 20°C 24 (as dry) Resin A (as used in Example 1) 36 Resin B (as used in Example 1) 30	105
50	maintained thereat for 13 hours.  166 parts of fluoroalkyl phthalate were obtained as a straw-coloured liquid having a fluorine content of 46.6%.	Di-iscoctyl phthalate 8 Triethylene glycol mono- pentadecafluorooctamoate (49.6% fluorine) (as pre- pared above) 2	110
55	Lacquer preparation  The liquid ester prepared above was incorporated into a lacquer having the following composition:—	Dibuyl and monobutyl acid phosphates (Equimolar mix- ture)  Solvent  300	115

Solvent

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	The solvent composition was: —	film made from the same composition except that the fluorine-containing compound was	60
	Parts	omitted.	
	Butyl acetate 30	Example 6	
		Fluorine-containing alkyl phthalate con-	
_	Ethyl sectors	enining 60% fluoring as prepared in Floring	
5		2 from the alcohol H(CrohaCrotor was	8
	66 O.P. Industrial Methyl-	made into a lacquer having the following for-	
	Xylene 15	mulation: — Parts	
	Toluene 15		
10	Ethylene glycol monoethyl	Nitroce)lulose (as used in Ex-	70
	ether 6	ample 1) 40 (as dry)	,,
	Culci	Resin A (as used in Ex-	
	m to mod to	ample 1) 40	
	The lacquer was sprayed on to wood to	Di-isooctyl phthalate 18	
	give a film with improved soil, water and	Pluoroalkyl phthalate contain-	
	grease resistance as compared with a film		75
15	made from the same composition from which	швоо /о т	
_	the fluorine-containing exter was omitted.	Solvent	
	hit 3122214 4	• • • • • • • • • • • • • • • • • • • •	
	Example 5	The solvent composition was:	
	The second containing paper		
	Preparation of fluorine-containing exter	Parts	
	20 parts of a polyethylene giycul having a	Butyl acetate 9	
<b>X</b>	molecular weight of about 800 and 21.60	Tabul acetate 25	80
	norte of pentadecafluorooctanoic acid were	Ethyl acetate 23	
	refluxed with 500 parts of dry towers in a	Butyl acetate 9 Ethyl acetate 25 n-butanol 5 Tokene 50	
	stirred reaction vessel filled with a porous	7	
	shimble containing anhydrous suchum supp-	Isopropanol	
5	ste in the reflux line. Reflux was maintained	•	
•	for 12 hours. The toluene was removed by	The lacquer was sprayed on to wood to	
	100 12 mours. The content was select in warno	sive a film which had improved soil, water	8:
	distillation and the product dried in vacuo	and grease resistance as compared with a film	
	to give 30 parts of polyethylene glycol penta-	made from the same composition from which	
	decaffuorooctanoste as a pale yellow inquit	made from the same composition from	
Ю	with a fluorine content of 12%.	the fluorine-containing ester was omitted.	
_	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	<b>.</b>	
	Lacquer preparation	REAMPLE 7	O.C
	The product prepared above was incorpor-	Preparation of fluorine-containing ester	90
	ated into a lacquer having the following com-	A fluoro-alcohol acid phosphate was pre-	
		pared in the following manner:—	
	position: —	35 parts of an alcohol having the formula	
	•	33 DRILLE OF ATT ATTRACTOR THE ATTRACTOR	
		THE PROPERTY OF THE PROPERTY O	
5	Pers	II/CED.CH.OH were mixed with 2 parts	94
5	Nitrocellulose as used in Ex-	h(CF), CH <sub>2</sub> OH were mixed with 3 parts phosphorus pentoxide and were heated under	95
5	Nitrocellulose as used in Ex-	phosphorus pentoxide and were heated under refure for 20 minutes, then diltered, giving a	95
5	Nitrocellulose as used in Ex- ample 1 except that the vis-	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then filtered, giving a filtrate having an acid value of 140 mg.	95
5	Nitrocellulose as used in Ex- ample 1 except that the vis- cosity of the solution of 40	phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g and containing a phosphate ester.	95
	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous accrone	phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which	
	Nitrocellulose as used in Rx- ample 1 except that the vis- cosity of the solution of 40 g. (dry) in aqueous accrone was 3 to 5 poises at 20°C 40 (as dry)	phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which	
	Nitrocellulose as used in Rx- ample 1 except that the vis- cosity of the solution of 40 g. (dry) in aqueous acctone was 3 to 5 poises at 20°C 40 (as dry) Resin A (as used in Ex-	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus penturide and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted	
	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acctone was 3 to 5 poises at 20°C  Resin A (as used in Example 1)  40	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial	
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io	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acetone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderafluorooctanosue (Fluorine content 12%) (as prepared above)  Solvent 12%  The solvent composition was:  Parts	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate escer. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lucquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Ex-	10
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40 45	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acetone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderaffuorooctanoate (Fluorine content 12%) (as prepared above)  Solvent 120  The solvent composition was:  Butyl acetate 9  Ethyl acetate 9  Ethyl acetate 25  n-butanol	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then filtered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lucquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  36	10
10 15	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acctone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderaffuorooctanosue (Phurine content 12%) (as prepared above)  Solvent 12% (as prepared above)  The solvent composition was:  Pasts  Butyl acetate 9  Ethyl acetate 9  Toluene 50	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then filtered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lucquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  Resin B (as used in Example 1)	10:
10 15	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acetone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderaffuorooctanoate (Fluorine content 12%) (as prepared above)  Solvent 120  The solvent composition was:  Butyl acetate 9  Ethyl acetate 9  Ethyl acetate 25  n-butanol	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then filtered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lucquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  Resin B (as used in Example 1)  36  Resin B (as used in Example 1)	10:
10 15	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acettone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderafinorooctanosus (Fluorine content 12%) (as prepared above)  Solvent 120  The solvent composition was:—  Parts  Butyl acetate 9  Ethyl acetate 9  Ethyl acetate 9  Ethyl acetate 5  n-butanol 5  Toluene 50  Isopropanol 11	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoxide and were heated under reflux for 20 minutes, then differed, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate escer. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lacquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  Resin B (as used in Example 1)  Oli-isooctyl phrhalate  10	100
10 15	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous accetone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1) 40  Polyethylene glycol pentaderaffuorooctanoate (Fluorine content 12%) (as prepared above) 24  Solvent 120  The solvent composition was:—  Pasts  Butyl acetate 9  Ethyl acetate 9  Ethyl acetate 9  Ethyl acetate 5  Toluene 50  Isopropanoi 11  The lacquer was sprayed on to cardboard	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoride and were heated under reflux for 20 minutes, then diltered, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate ester. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lizequer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  ——  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  Resin B (as used in Example 1)  Johnsooctyl phrhalate  Fluoro-alcohol mixed acid	10:
40 45	Nitrocellulose as used in Example 1 except that the viscosity of the solution of 40 g. (dry) in aqueous acettone was 3 to 5 poises at 20°C 40 (as dry)  Resin A (as used in Example 1)  Polyethylene glycol pentaderafinorooctanosus (Fluorine content 12%) (as prepared above)  Solvent 120  The solvent composition was:—  Parts  Butyl acetate 9  Ethyl acetate 9  Ethyl acetate 9  Ethyl acetate 5  n-butanol 5  Toluene 50  Isopropanol 11	H(CF <sub>1</sub> ), CH <sub>2</sub> OH were mixed with 5 parts phosphorus pentoxide and were heated under reflux for 20 minutes, then differed, giving a filtrate having an acid value of 140 mg. KOH/g. and containing a phosphate escer. The ester was orthophosphoric acid in which one or two hydrogen atoms were substituted by a fluoro-alcohol group, giving a partial ester.  Lacquer preparation  The phosphate prepared above was incorporated into a lacquer composition having the following composition:  Parts  Nitrocellulose (as used in Example 1)  Resin A (as used in Example 1)  Resin B (as used in Example 1)  Oli-isooctyl phrhalate  10	100

	1,1	57,320	5
	The column had the following comment	*	
	The solvent had the following composi-	Рапь	
	10dt. —	Acetone 50	
	Parts	Ethyl acotate 15	
		Toluene 15	60
5	Butyl acetate 30 Ethyl acetate 18	66 O.P. Industrial Methyl-	
,	n-butanol 12	ated Spirits 15	
		Ethyl lactate 5	
	66 O.P. Industrial Methyl- ated Spirits 4	The leagues lind . M	
	ated Spirits 4  Xylene 15	The lacquer was applied to cardboard by	
IJ	Toluene 15	brushing and gave a film with improved soil,	65
10		water and grease resistance in comparison with	
	Ethylene glycol monoethyl ether 6	a film from the same composition but from	
	etuet	which the fluorine-containing ester was omitted.	
	The lacquer was brushed on to wood and	VIIIIIIII.	
	gave a film with improved soil, water and	The same n 10	
15		BXAMPLE 10	70
1.3		Resin C used in this Example was a castor	
	made from the same lacquer composition	oil alkyd containing 45% fatty scid, 41%	
	from which the fluorine-containing ester was omitted.	phthalic anhydride and having an acid value	
	minica.	40-47 mg. KOH/g. A 50% solution in	
	Drivers 0	xylene had a viscosity of 36-60 poises at 20°C.	75
20	EXAMPLE 8		
20	A lacquer baving the following composi-	A lacquer of the following composition	
	tion was prepared:—	was prepared:—	
	Parts	Dame	
	Cellulose acetate powder hav-	Cellulose acotate butyrate	-
	ing an acetyl value of 35% 70	containing approximately	BO
25	Trichlogoethyl phosphate 30	37% butyryl, 13% sceryl	
	Fluorine-containing alkyl		
	phthalate containing 60%	To	
	fluorine (as prepared in Ex-	Pentacrythritol triscetate	
	ample 2) 1.7	monopenta decada vorocctaronte	85
30	Solvent 400	(fluorine content 43%) (as pre-	
	5017411		
	The solvent composition was:		
	+	Dunnel	-
	Perts	66 O.P. Industrial Methyl-	90
	Acetone 50	attal Spirits 7	
	Ethyl scenate 15	Butyl accepte 16	
35	Toluene 15	Ethylene glycol monoburyl	
	66 O.P. Industrial Methyl-	ether 5	95
	ated Spirits 15	Ethylene glycol monobusyl	30
	Ethyl lactate 5	ether acetate 3	
	The lacquer was applied to cardboard by	3	
40	brushing and gave a film with improved soil,	The resultant facquer was approved on to a	
	water and oil resistance as compared with a	position surface and core a file	
	film made from the same composition from	WILLIA WAS SUPERIOR IN SAIL TROOPS and manage	100
	which the fluorine-containing ester was	TOROUGHE TO B DIM MADE From the same com-	100
	omitted.	position from which the fluorine-containing	
	· _	ester was canimed.	
45	EXAMPLE 9	•	
	A lacquer having the following composi-	EXAMPLE 11	
	tion was prepared:	The ethyl cellulate used in this Bosenia	105
	_	CARRIEDE 47.3 TO 49.0% (Chincy) A contrion	
	Pants	CE 3 8. III 100 CC. Of I mightine of 20 year	
-	Cellulose acetate powder hav-	differ toxicite and 20 volumes ethanol and a	
50	ing an acetyl value of 35% 70	VISCOSITY OF S TO 11 DESTRIBUTIONS OF 75°C	
	Trichloroethyl phosphate 30	the Resin D used in this Framela was	110
	Penmerythritol triocetate	CERTIFIE TUZ, & MODINES DERIVATIVE PRINTERS	
	monopentadecaffuorooctanoate	UI FUSID, DEVING AN ACID VANIE OF 35 mg	
	(as prepared in Example 1) 2.2	NORTH B. (CENOLYN 18 a registered Trade	
55	Solvent 400	Mark).	
	70t - 4.4	A facquer having the following composition	115
	The solvent composition was:—	was prepared:	

õ	1,157,320		
<del></del> .			
5	Parts Ethyl cellulose 18 Dicyclohexyl phthalate 3.4 Resin D 4.5 Pentaerythritol triacctate monopentadecafluorooctanoate (or prepared in Faxmole 1) 3	The resultant lacquer was sprayed on 40 wood and gave a film with improved soil, water and grease resistance as compared with a film made from the same composition from which the fluorine containing ester was omitted.  Example 14	65
10	(as prepared in Eaxaple 1) 3 Toluene 42 66 O.P. Industrial Methylated Spirits 10.6 Xylene 14 Butanol 3.5	Preparation of fluorine-containing ester 37.36 parts of castor oil, 16.56 parts of pentudecafluorooctanoic acid and 10 parts of tylene were added to a stirred reaction vessel fitted with a gas inlet and a porous thimble containing anhydrous sodium sulphate in the	70
15	The resultant lacquer was sprayed on to cardboard and gave a film of improved soil, water and grease resistance as compared with a film made from the same composition but from which the fluorine-containing compound is omitted	reflux line. Carbon dioxide gus was passed in at a rate of 10 cc. per minute and the vessel contents heated to reflux and maintained thereat for 4 hours.  Xylene was removed under vacuum to give 45.3 parts of a pale yellow liquid having a fluorine content of 20%.	75 80
20	Example 12 A lacquer of the following composition was prepared:—	Lacquer preparation A lacquer of the following composition was prepared:—	٠
25	Parts Ethyl cellulose (as used in Example 11) Dicycloheryl phthalate Result D (as used in Example 11) 4.5	Pants Nicrocellulose as used in Hz- ample 1 but of viscosity such that 20 g. (dry) dis- solved in 100 cc. of a mixture	85
<b>3</b> 0	ample 11) Finerine-containing alkyl phthalate containing 60% fluorine (as prepared in Ex- ample 2) Toluene  42	of 95 volumes acetone and 5 volumes water was between 25 and 45 poises at 20°C 10 (as dry) Blown linseed oil 90 poise viscosity at 20°C 8	90
35	66 O.P. Industrial Methylated Spirits 10.6  Xylene 14  Butanol 3.5	Blown castor oil 90 poise viscosity at 20°C 4.5 Fluorine-containing castor oil ester (as prepared above) 2.5 Solvent 70	95
40	The regulant lacquer was sprayed on to cardboard and gave a film of improved soil, water and grease resistance as compared with a film made from the same composition but from which the fluorine-containing compound is omitted.  Example 13  A lacquer of the following composition was prepared:—	The solvent composition was:—  Pares  Buryl accente 15 n-butanol 10 Ribyl accente 20 Isopropanol 9 Methyl cyclohexanoue 10 Tohuene 36	100
50	Parts Vinylite VYHH (Vinylite is a Registered Trade Mark) (A polyvinyl chloride/ polyvinyl acetate copolymer comaining 83% vinyl chloride and hav- ing an intrinsic viscosity in	When sprayed on leather the film formed showed improved soil, water and grease resistance as compared with a film from the same composition but omitting the fluorine-containing ester.  EXAMPLE 15	110
55	cyclohexanone at 20°C or 0.53) 20 Penmerythritol triacetate monopermadeculfuorooctanoate	A lacquer of the following composition was prepared:  Parts  Nitrocellulose (as used in	115
60	(as prepared in Example 1) 2 Toluene 40 Methyl ethyl ketone 20 Methyl isobutyl ketone 20	Example 14) 30 (as dry) Tetanium dioxide 21 Solvent (as used in Example 14) 217.5	120

Rlown linseed oil 90 poises 16.8 Rlown caster oil 90 poises 9.5

The resultant lacquer was divided and to one half were added 2 parts of the fluorinated castor oil ester prepared in Example 14 and to the other half were added 2 parts of ordinary castor oil.

10 of ordinary castor oil.

The formulations were sprayed on to leather to form films. The film containing the fluorinated castor oil ester was superior in soil, water and greate resistance to that 15 containing ordinary castor oil.

EXAMPLE 16
A lacquer of the following composition was prepared:—

		Parts
20	Nitrocellulose (as used in	
	Example 14)	-28.6
	Dibutyl phthelete	4
	Dicyclohexyl phthalate	Ś.S
	Castor oil	0.7
25	Fluorine-containing caster	oli
	ester (as prepared in Ex-	
	graple 14)	3.3
	74 O.P. Industrial Methy	b-
	ated Spirits	26.1
30	Ethyl acctate	21.4
	Butyl acetate	5.2
	n-butanoi	5.2
	The lacquer, applied to pa	

and grease resistance to a film made from a lacquer of the same composition from which the fluorine-containing ester was omitted.

EXAMPLE 17

Preparation of fluorine-containing ester

30 parts trimethylol amino methane ('tris amino'), 50 parts lauric acid and 20 parts tylene were mixed in a 3-necked stirred reaction flusk fitted with a gas inlet and a Dean and Stark apparatus. Carbon dioxide gas was passed in at a rate of 10 cc. per minute and the mixture in the flask heated at 200°C for 1 hour. After cooling to 120°C, a further 50 parts lauric acid were added and again the contents of the flask were heated at 200°C for 1½ hours. The xylene was removed by vacuum distillation to give a pale yellow liquid. a lauric 'diester'

vacuum distillation to give a pale yellow liquid, a launic 'diester'.

4.7 parts of this 'diester', 4.0 parts penta-decafluorooctanoic acid and 15 parts xylene were mixed in a 3-necked stirred reaction flask fitted with a gas inlet and condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the mixture was heated under reflux for 4 hours. The xylene was removed by vacuum distillation to give fluorin-

ated exaceline as a cream coloured, waxy solid having an acid value of 15 mg. KOH/g. and a fluorine content of 30.6%.

The product had the formula:—

where R=lantyl group and R'=pentadecaffuoroocumyl group

Lacquer preparation

The product prepared above was incorperated in a lacquer of the following composition:—

Nitrocellulose (as used in	Parts	
ample 1) Resh A (as used in Ex-	40	75
ample 1) Di-iscocryl phthelate	40 10	.,
Pinorinated oxazoline as described above Solvent (as used in Examp	10 ole	80
6	150	

The lacquer was sprayed on to wood. The resultant film was superior in soil, water and grease resistance to a film prepared from the same lacquer composition from which the 85 fluorinated oxazoline was omitted.

A facquer of the following composition was prepared:—

Parts	90
Titanium dioxide 6.2	
Carbon black 0.1	
40% solution in a mixture of	
50 Volumes accione and 70	
volumes toluene of polymethyl	05
methacrylate of inherent vis-	
cosity 0.34	
Ethylene glycol monoethyl	
ether acetate 2.5	
The above ingredients were ball milled for	100
24 hours and there were then added the fol-	100
lowing: —	
Parts	
40% solution of polymethyl	
methacrylate as used above 17.9	105
Buryl benzyl phrhalate 3.0	103
Fluoroalkyl phthalate commin-	
ing 60% fluorine (as prepared	
Ribulate almol monaghil at	
Ethylene glycol monoethyl ether	110

acetate

Tolucia

methyl ethyl kerone

100

Ŗ

20

The lacquer was sprayed on to metal and gave a film with improved soil, water and grease resistance as compared with a film prepared from the same lacquer composition from which the fluorinated ester was omitted.

EXAMPLE 19

A lacquer was prepared in the same way as for example 18 but in place of the fluoro-alkyl phthalate containing 60% fluorine, 0.80 parts of pentaerythritol triacetate monopentadecafluorocctanoate (43% fluorine) as used in Example 1 were used. The resulting lacquer was sprayed on to wood and gave a film with improved soil, water and grease resistance as compared with a film prepared from the same lacquer composition but omitting the fluorinated pentacrythritol ester.

BEAMPLE 20

The rosin used in this Example was a commercial rosin consisting essentially of about 90% of rosin acids. These are isomeric C. acids (such as, for example, abietic acid) containing the phenanthrene nucleus.

The resin E used in this Example was a rosin/maleic anhydride condensate esterified with glycerol having an acid value less than 32 mg. KOH/g.

Preparation of fluorine-containing ester

40 parts of fluorinated alcohol of formula
H(CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH, 30 parts of commercial
rosin and 0.05 parts of sulphuric acid were
mixed in a street reaction vessel fitted with a stirrer, gas inlet and a reflux condenser. Carbon dioxide was passed in at a rate of 10 cc. per minute and the vessel contents were heated and allowed to reflux at 170°C until the acid value fell below 40 mg. KOH/

g. (approximately 13 hours).
The excess alcohol was then distilled off. The vessel contents were cooled, extracted with water and finally dried under vacuum to give 62 g. of a fluorinated rosin ester as a hard, transparent, yellow, brittle solid.

Lecquer preparation A lacquer of the following composition was prepared:-

		Parts
	Nitrocellulose (as used	in Ex-
	ample 1)	12.3
50	Pluorinated rosin ester	(pre-
JU	pared as above)	13.3
	Resin E	8.6
	Dibutyl phthalate	1.8
	Buryl acctate	25.0
		40.0
55	Toluens	21.0
	Methyl ethyl ketone	
	Methyl isobutyl ketone	14.0

The lacquer was sprayed on to wood. The resulting film had a better water and oil

repellency and better sail and stain resistance 60 than a film prepared from the same lacquer composition from which the fluorine-containing rosin ester was amuted.

REAMPLE 21

Preparation of fluorine-containing ester

22.5 parts of rosin, 45.0 parts of fluorinecontaining alcohol of formula H(CR<sub>2</sub>)<sub>0</sub>CH<sub>4</sub>OH and 0.05 parts of sulphuric acid were
mixed in a reaction vessel fitted with a grirrer,
mixed in a reaction vessel fitted with a grirrer, gas inlet and a reflux condenser. Carbon dioxide was passed in at a race of 10 cc. per minute and the vessel contents were heated and allowed to reflux at 235 °C until the acid

value fell below 20 mg. KOH/g.

The excess alcohol was then distilled off.

The vessel contents were cooled, extracted with water and finally dried under vacuum to give 62 g. of a fluorinated rosin ester as a hard, yellow solld.

Lacquer preparation A lacquer of the following composition was prepared:-

	Perts	
Nitrocelhilose (as used in ample 1)	123	85
Fluorinated rosin ester (propared as above)	13.3	
Resin E (as used in Exam 20)	nple 8.6	
Dibutyl phthalate	1.8 25.0	90
Butyl acetate Toluene	40,0	
Methyl ethyl ketone Methyl isobutyl ketone	21.0 14.0	
MEMAT ISOPHIAL PERME		•

The lacquer was sprayed on to wood. The resulting film had a higher water and oil repellency and better soil and stain resistance than a film made from the same lacquer composition from which the fluorinated rosin ester was omitted.

EXAMPLE 22

Preparation of fluorine-containing cater
42.5 parts rosin as used in fixample 20
and 2.5 parts of maleic anhydride were mixed
in a started reaction vessel fitted with a gas
inlet and reflux condenser. Carbon dioxide
was passed in at a rate of 10 cc, per minute
and the temperature raised to 180°C and
maintained the reset for 1 hour. maintained therest for I hour.

The vessel contents were cooled to below 110 100°C and 76 parts of a fluorine-containing alcohol of formula H(CR)<sub>m</sub>CH<sub>2</sub>OH were added. Heating was resumed and the temperature maintained at reflux until the acid value fell below 40 mg KOH/g.

98 parts of fluorinated maleinised rosin ester were obtained as a hard, yellow, brittle

solid.

		Parts	
5	Nitrocellulose (as used in Ex-		
-	ample 1)	12.3	
	Phoringted maleinised rosi	a	
	ester (prepared as above)	8.6	
	Exter gum (glycerol exter		
10	of rosin)	13.3	
	Dibutyl phthelate	1.8	
	Butyl acetate	25.0	
	Toluene	40.0	
		•	
	Methyl ethyl ketone	21.0	
15	Methyl isobutyl ketone	14.0	

A lacquer of the following composition

Lacquer preparation

was prepared:

The lacquer was sprayed on to metal. The resultant film was superior in soil, water and grease resistance to a film prepared from the same lacquer composition but omitting the fluorinated ester.

#### EXAMPLE 23

The nitrocellulose used in the Example had a nitrogen content between 11.2 and 11.8% and was 'damped' with isopropanol in the ratio of 70 parts nitrocellulose to 30 parts isopropanol, 40 g. of this nitrocellulose dried and dissolved in 100 cc. aqueous actione, prepared by mixing 95 volumes acceptant of 50 poises at 20°C.

Preparation of fluorine-contain ester

\$\beta\$-perfluorotrialkyl propionic acid having the formula (C.F.)\(\text{c}(C.F.)\(\text{c}(C.F.)\(\text{c}(C.F.)\)\(\text{c}(C.F.)\(\text{c}(C.F.)\)\(\text{c}(C.F.)\(\text{c}(C.F.)\)\(\text{c}(C.F.)\(\text{c}(C.F.)\)\(\text{c}(C.F.)\(\text{c}(C.F.)\)\(\text{c

5 parts of the acid were mixed with 10 parts of purified thionyl chloride and heared under reflux for 2 hours a 45°C and a further 4 hours at 75°C. Excess thionyl chloride was distilled off, leaving a residue of β-perfluorotrialkyl propionyl chloride.

0.5 parts of sodium metal were reacted with 5 parts of the monoethyl ether of dicthylene glycol in 35 parts of toluene and the solution was added to the β-perfluoro-

trialkyl propionyl chloride prepared above. The resulting mixture was heated to  $115^{\circ}$ C for 6 hours and the toluene was distilled off at atmospheric pressure. The residue was distilled under reduced pressure and a fraction of the distillate collected in the boiling range 55—85°C at a pressure of 2 mm. This fraction was redistilled and gave the ester of diethylene glycol monoethyl ether and  $\beta$ -trifluoromethyl bis( $\beta$ -pentalluoroethyl)propionic acid boiling at 75—80°C at 1 mm. and containing 39% fluorine.

Lacquer preparation
A lacquer of the following composition was prepared: —

	Parts	
Nitrocellulose	10 (as dr	<b>7</b> )
Fluorinated ester (as p	repared `	•
above)	1	
Ethyl acetate	25	80
n-butyl acetate	25	
n-butyl alcohol	10	
Toluene	40	

This lacquer was applied to cardboard and gave a film with improved soil, water and grease resistance as compared with a film from the same composition from which the fluorinated ester was omitted.

Example 24	
Parts	90
Athyl cellulose (as used in	
Example 11) 20	
Phorinated ester (as prepared	
in Example 23)	
74 O.P. Industrial methy-	95
lated Spirits 20	
Tohiene 80	

This lacquer was applied to cardboard and gave a film with improved soil, water and grease resistance as compared with a film 100 from the same composition from which the fluorinated ester was omitted.

EXAMPLE 2	)	
	Parts	
Cellulose acetate (as used	ì	105
in Example 9)	15	
Fluorinated ester (as prep	pared	
in Example 23)	0.4	
Acctone	50	
Ethyl acetate	15	110
74 O.P. Industrial Methy	/L	110
ated Spirits	15	
Ethyl lactate	* 7	•
Trans- success	,	

This lacquer was applied to cardboard and gave a film with improved soil, water and 115 grease resistance as compared with a film from the same composition from which the fluorinated ester was omitted.

It is to be noted that the fluorine-containing esters which may be included in the film-forming compositions of the present invention are not formed by condensation polymerisation and therefore are not to be confused with the polymeric fluorine-containing condensation esters used in the compositions described and claimed in our co-pending Application No. 11955/67 (Serial No. 1157319).

#### WHAT WE CLAIM IS:-

A film-forming composition comprising
a film-forming polymeric material and a
fluorine-commining ester containing a chain of
 at least 3 carbon atoms in which at least
half of the carbon valencies other than carbon to carbon are satisfied by a fluorine atom,
the quantity of ester being such that the
fluorine content of the composition is in the
 range of 0.1 to 30%.

2. A composition as claimed in Claim 1 wherein the fluorine-containing ester is derived from a fluorine-containing carboxylic acid of the formula R\*—COOH wherein R\* denotes a fluorinated alkyl group.

3. A composition as claimed in Claim 2 wherein the R<sup>p</sup> group is a straight or branched chain alkyl group of 4 to 18 carbon atoms in which at least half of the hydrogen atoms are replaced by fluorine atoms.

4. A composition as claimed in Claim 2 or Claim 3 wherein the R<sup>p</sup> group is a perfluorobutyl or a perfluorobetyl or a bis(2-pentafluorocthyl)2 - trifluoromethyl ethyl

5. A composition as claimed in any one of Claims 1 to 4 wherein the fluorine-containing ester is an ester of castor oil, ethylene glycol, polyethylene glycol, glycerol, trimethylolpropane, trimethylolethane, mono- and dipentaerythritol, trimethylol amino methane or diethylene glycol monoether.

6. A composition as claimed in Claim 1 wherein the fluorine-containing ester is derived from an alcohol containing fluorine 45 atoms.

7. A composition as claimed in Claim 6 wherein the fluorine-containing easer is derived from an alcohol of the formula R\*(CH<sub>2</sub>)<sub>n</sub>OH wherein R\* denotes a fluorinated alkyl group and n is an integer from 1 to 3.

8. A composition as claimed in Claim 7 wherein the R<sup>p</sup> group of the alcohol is a straight or branched chain alkyl group of 3 to 18 carbon atoms wherein at least half of the hydrogen atoms are replaced by fluoring atoms.

 A composition as claimed in Claim 8 wherein the R<sup>F</sup> group is a perfluoropropyl, perfluorobutyl, perfluorohexyl, perfluoroccyl or a perfluorodecyl group.

10. A composition as claimed in any one of Claims 7 to 9 wherein the fluorine-containing ester is an ester of phosphoric, phthalic, adipic, sebacic, tartaric, citric, stearic or abetic acid, or the adduct of abietic acid and maleic anhydride or the carboxylic acid of the formula R\*—COOH wherein R\* denotes a fluorinated alkyl group.

11. A composition as claimed in any one of Claims 1 to 10 wherein the film-forming polymeric material comprises nitrocellulose, cellulose acetate butyrate, ethyl cellulose, polymethyl methacrylate, polyvinyl chioride, polyvinyl acetate or copolymers thereof.

12. A film-forming composition substantially as herein described with reference to any of the Examples.

13. A lacquer solution comprising a filmforming composition as claimed in any one of Claims 1 to 12,

THOMAS J. REID, Agent for the Applicants.

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